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Transmitted herewith for filing Under Rule 1.53(f) is the **Patent Application** of:

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For: METHODS OF PROCESSING AND SYNTHESIZING ELECTRICALLY CONDUCTIVE
POLYMERS AND PRECURSORS THEREOF TO FORM ELECTRICALLY CONDUCTIVE
POLYMERS HAVING HIGH ELECTRICAL CONDUCTIVITY

Enclosed are:

- ☒ 5 sheets of informal drawings.
- ☐ An assignment of the invention to International Business Machines Corporation, Armonk, New York 10504.
- ☐ A certified copy of a _____ application.
- ☐ An associate power of attorney.

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Respectfully submitted,

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**METHODS OF PROCESSING AND SYNTHESIZING ELECTRICALLY CONDUCTIVE
POLYMERS AND PRECURSORS THEREOF TO FORM ELECTRICALLY CONDUCTIVE
POLYMERS HAVING HIGH ELECTRICAL CONDUCTIVITY**

FIELD OF THE INVENTION

The present invention is directed to methods of processing and synthesizing electrically conductive polymers and precursors thereof to form electrically conductive polymers having high electrical conductivity.

BACKGROUND

Electrically conductive organic polymers have been of scientific and technological interest since the late 1970's. These relatively new materials exhibit the electronic and magnetic properties characteristic of metals while retaining the mechanical properties associated with conventional organic polymers. Herein we describe electrically conducting polymers and precursors thereof, for example substituted and unsubstituted polyparaphenylene vinylenes, polyparaphenylenes, polyanilines, polythiophenes, polyazines, polyfuranes, polypyrroles, polyselenophenes, poly-p-phenylene sulfides, polythianaphthenes, polyacetylenes, combinations thereof and blends thereof with other thermoplastic and thermoset polymers and copolymers of the monomers thereof. These polymers are conjugated systems which are made electrically conducting by doping. The non-doped or non-conducting form of the polymer is referred to herein as the precursor to the electrically conducting polymer. The doped or conducting form of the polymer is referred to herein as the conducting polymer.

Conducting polymers have potential for a large number of applications in such areas as electrostatic charge/ (ESC/ESD) protection, electromagnetic interference (EMI) shielding, resists,

electroplating, corrosion protection of metals and ultimately metal replacements, i.e. wiring, plastic microcircuits, conducting pastes for various technologies (solder alternative) etc.. Many of the above applications especially those requiring high current capacity have not yet been realized because the conductivity of processable conducting polymers is not yet adequate for such applications. In order for these materials to be used in place of metals in more applications, it is desirable to increase the conductivity of these materials. In addition, the processability of these polymers also requires improvement. Although some these polymers are soluble, the solubility is generally limited and the solutions tend to be not stable over time.

The polyaniline class of conducting polymers has been shown to be one of the most promising and most suited conducting polymers for a broad range of commercial applications. The polymer has excellent environmental stability and offers a simple, one-step synthesis. However, the conductivity of the material in its general form (unsubstituted polyaniline doped with hydrochloric acid) is generally on the low end of the metallic regime most typically, on the order of 1 to 10 S/cm (A.G. Macdiarmid and A.J. Epstein, Faraday Discuss. Chem. Soc. 88, 317, 1989). In addition, the processability of this class of polymers requires further improvement. Although polyaniline is a soluble polymer, it has been noted that the solutions tend to be unstable with time (E.J. OH et al, Synth. Met. 55-57, 977 (1993). Solutions of for example the polyaniline in the non-doped form tend to gel upon standing. Solutions greater than 5% solids concentration tend to gel within hours limiting the applicability of the polymer. Solubility of the doped, conducting form has generally been less than that observed with the non-doped form. It is desirable to devise methods of increasing the conductivity of the doped polyanilines and to enhance the processability of these systems to allow broader applicability.

The conductivity (σ) is dependent on the number of carriers (n) set by the doping level, the charge on the carriers (q) and on the mobility (μ) (both interchain and intrachain mobility of the carriers).

processing the conducting polymer or conducting polymer precursor by using selected solvents which can effectively solvate the polymer chains to allow higher levels of conductivity to be achieved are described.

OBJECTS

It is an object of the present invention to process electrically conductive polymers and precursors thereof to result in polymers having substantially enhanced electrical conductivity.

It is an object of the present invention to process electrically conducting polymers and precursors thereof to result in polymers having high solubility.

It is an object of the present invention to process electrically conductive polymers and precursors thereof in appropriate solvents which are capable of effectively solvating the chains to give rise to materials having high electrical conductivity and good solubility..

It is an object of the present invention to attain highly conducting electrically conducting polymers and precursors thereof by using appropriate solvents capable of effectively solvating the polymer chains during the synthesis of the polymer.

It is an object of the present invention to process conducting polymer precursors in these selected solvents so as to achieve more uniform doping .

It is an object of the present invention to process conducting polymer precursors and conducting polymers in these selected solvents so as to achieve high solubility and good solution stability.

It is an object of the present invention to process conducting polymer precursors and conducting polymers in these selected solvents so as to better process these polymers into films, fibers, or any structural form.

It is an object of the present invention to deaggregate aggregated molecules which are precursors to the electrically conducting polymers or so that the molecules can be more processed into films, fibers, or any structural form having tunable morphology and mechanical/physical properties

It is an object of the present invention to deaggregate aggregated molecules which are electrically conducting polymers.

It is an object of the present invention to deaggregate aggregated molecules which are electrically conducting polymers so that the molecules can exhibit good processability and good solution stability.

It is an object of the present invention to deaggregate aggregated molecules which are electrically conducting polymers so that the molecules can be more effectively processed into films, fibers, or any structural form.

It is an object of the present invention to deaggregate aggregated molecules which are electrically conducting polymers so that the molecules can be more effectively processed into films, fibers, or any structural form having tunable morphology and mechanical/physical properties.

It is an object of the present invention to increase the electrical conductivity of electrically conductive polymers.

It is another object of the present invention to increase the electrical conductivity of electrically conductive polymers by extending the electrically conductive regions or islands of the electrically conductive polymer.

It is another object of the present invention to further increase the electrical conductivity of a deaggregated electrically conductive polymer by stretch orientation.

SUMMARY OF THE INVENTION

A broad aspect of the present invention is a method of processing electrically conducting polymers or precursors thereof or synthesizing electrically conducting polymers or precursors thereof in appropriate solvents which effectively solvate the polymer chains so as to result in polymers having high electrical conductivity, good solubility, and good solution stability.

A more specific aspect of the present invention is a method of processing electrically conducting polymers or precursors thereof providing better processability of these polymers into films, fibers or structural forms which exhibit high electrical conductivity.

A more specific aspect of the present invention is a method of effectively solvating electrically conducting polymers or precursors thereof resulting in films, fibers, or structural forms having tuned morphology.

A more specific aspect of the present invention is a method of effectively solvating electrically conducting polymers or precursors thereof resulting in films, fibers or structural forms having larger electrically conducting regions or islands in the electrically conducting polymer.

A more specific aspect of the present invention is a method of effectively solvating electrically conducting polymers or precursors thereof resulting in films, fibers, or structural forms having deaggregated polymer chains.

A more specific aspect of the present invention is a method of effectively solvating electrically conducting polymers or precursors thereof resulting in films, fibers, or structural forms having high crystallinity.

A more specific aspect of the present invention is a method of fabricating electrically conducting polymers and precursors thereof that are deaggregated; deaggregated polymer exhibits increased solubility processability, higher conductivity upon doping, and more uniform doping than do the corresponding aggregated polymers.

A more specific aspect of the present invention is a method of providing well solvated electrically conducting polymers having application for electrodes for displays and devices, electromagnetic interference shielding, electrostatic charge/discharge protection, corrosion protection, resists, and circuits.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a general formula for a polyaniline; (a) is the precursor form of the polymer or the non-doped form of the polymer; (b) is the doped form of the polymer or the electrically conducting form of polyaniline; (c) is the actual structure for the doped electrically conducting polymer consisting of a polysemiquinone radical cation.

Fig. 2 depicts interchain hydrogen bonding in emeraldine base between an amine site of one chain and an imine site of a second chain.

Fig. 3 depicts a ultraviolet/visible/near IR spectra for a polyaniline doped with acrylamidopropanesulfonic acid processed from a mixture of hexafluoroisopropanol and hexafluorophenylpropanol (50/50); A highly delocalized polaron absorption observed.

Fig. 4 depicts a ultraviolet/visible/near IR spectra for the same polyaniline doped material as in Fig. 3 but processed from NMP. A localized polaron absorption observed.

Fig. 5 depicts a ultraviolet/visible/near IR spectra for polyaniline doped material processed from hexafluoroisopropanol that shows the concentration effect. At 2%, a stronger localized polaron peak is observed indicating increased interchain interactions as compared to the 1%.

Table 1 depicts Examples of Doped Polyanilines in Suitable Solvents Giving High Conductivity

Table 2 depicts EMI Shielding results on the polyaniline acrylamidopropanesulfonic acid coatings processed from hexafluoroisopropanol/hexafluorophenylpropanol.

Further objects, features, and advantages of the present invention will become apparent from a consideration of the following detailed description of the invention when read in conjunction with the drawing FIGs., in which:

DETAILED DESCRIPTION

The present invention is directed to methods of processing electrically conducting polymers or precursors thereof resulting in high electrical conductivity, good solubility, and good solution stability. Examples of such polymers that can be used to practice the present invention are substituted and unsubstituted polyparaphenylenes, polyparaphenylenevinyls, polyanilines, polyazines, polythiophenes, polythianaphthenes, poly-p-phenylene sulfides, polyfuranes, polypyrroles, polyselenophenes, polyacetylenes formed from soluble precursors and combinations thereof and copolymers of monomers thereof. The general formula for these polymers can be found in U.S. Patent 5,198,153 to Angelopoulos et al. the teaching of which is incorporated herein by reference. The present invention will be described with reference to one type of polymer which is a substituted or unsubstituted polyaniline or copolymers of aniline with other monomers having the general formula shown in Fig. 1 wherein each R can be H or any organic or inorganic radical; each R can be same or different; wherein each R¹ can be H or any organic or inorganic radical, each R¹ can be the same or different $x \geq 1$; preferably $x \geq 2$ and y has a value from 0 to 1. Examples of organic radicals are alkyl or aryl radicals. Examples of inorganic radicals are Si and Ge. This list is exemplary only and not limiting.

The precursor to the electrically conducting polymer form is shown in Fig. 1a. This is the non-doped form of the polymer or the base polymer. Fig. 1b shows polyaniline doped with a

dopant. If the polyaniline base is exposed to cationic species QA, the nitrogen atoms of the imine part of the polymer become substituted with the Q^+ cation to form an emeraldine salt as shown in Fig. 1b. Q^+ can be selected from H^+ and organic or inorganic cations, for example, an alkyl group or a metal. QA can be a protic acid where Q is hydrogen. When a protic acid HA is used to dope the polyaniline, the nitrogen atoms of the imine part of the polyaniline are protonated. The emeraldine base form is greatly stabilized by resonance effects. Charges distribute through the nitrogen atoms and aromatic rings making the imine and amine nitrogens indistinguishable. The actual structure of the doped form is a delocalized polysemiquinone radical cation as shown in Fig. 1c.

Polyaniline can exist in a number of oxidation states. The emeraldine form of the polymer refers to the material that consists of approximately equal number of benzenoid units and quinoid units ($y=0.5$ in Fig. 1). The emeraldine polymer can be reduced to the leucoemeraldine polymer where $y=1$ in Fig. 1. The leucoemeraldine base form of the polymer is not stable in ambient conditions. The emeraldine polymer can be oxidized to the pernigraniline form where $y=0$; however, the fully oxidized form of the polymer also tends not to be stable. In principle, other oxidation states intermediate between $y=0$ and $y=1$ are possible. The emeraldine base form of the polyaniline is the most stable form. Because of its environmental stability, it is the form of polyaniline that has been the most abundantly studied and is the form that is suited for technological applications. The most preferred embodiment of the present invention is the emeraldine base form of the polyaniline wherein y has a value of approximately 0.5.

The emeraldine base form of polyaniline is soluble in various organic solvents and in various aqueous acid solutions. Examples of organic solvents are dimethylsulfoxide (DMSO), dimethylformamide (DMF), N-methylpyrrolidinone (NMP), N,N'-dimethyl propylene urea (DMPU), pyridine, m-cresol, phenol and so on. This list is exemplary only and not limiting. Examples of aqueous acid solutions are aqueous acetic acid and formic acid solutions. This list is exemplary only and not limiting.

form giving rise to a more deaggregated structure, a structure having more expanded chains, and a more crystalline structure. It is found that fluorinated polar solvents either alone or in combination with other fluorinated solvents or with other non fluorinated solvents are effective solvents for the polyaniline.

A non limiting exemplary list of fluorinated solvents useful to practice the present invention include:

(Fluorinated Alcohols or Phenols)

Hexafluoroisopropanol

Tetrafluoropropanol

Pentafluoropropanol

Hexafluorophenylpropanol

Perfluorobutyl alcohol

Octafluoropentanol

Hexafluoro-2-propanol

Pentafluoro-1-Propanol

Tetrafluorophenol

Trifluorophenol

Difluorophenol

Tetrafluoro-1-Propanol

4-(Trifluoromethyl)benzyl alcohol

2,2,2- Trifluoroethanol

2,4,5 Trifluorophenol

2,4 Difluorobenzyl alcohol

2,4 Difluorophenol

4-Fluorobenzyl alcohol

Other examples of fluorinated alcohols or phenols include:

2,2,3,3,3-pentafluoro-1-propanol, 2 -(perfluorobutyl)ethanol,

2-(perfluorohexyl)ethanol, 2-(perfluorooctyl)ethanol, 2-(perfluorodecyl)ethanol, 2-(perfluoro-3-methylbutyl)ethanol, 1H,1H,3H-tetrafluoro-1-propanol, 1H,1H,5H-octafluoro-1-pentanol, 1H,1H,7H-dodecafluoro-1-heptanol, 1H,1H,9H-hexadecafluoro-1-nonanol, 2H-hexafluoro-2-propanol or 1H,1H,3H-hexafluoro-2-butanol;

(Fluorine containing acids)

trifluoroacetic acid, perfluoropropanoic acid, perfluorobutanoic acid, perfluoropentanoic acid, perfluorohexanoic acid, perfluoroheptanoic acid, perfluorooctanoic acid, perfluorononanoic acid, perfluorodecanoic acid, 3H-tetrafluoropropanoic acid, 5H-octafluoropentanoic acid, 7H-dodecafluoropentanoic acid or 9H-hexadecafluorononanoic acid, an amide of such a fluorine-containing carboxylic acid, trifluoromethanesulfonic acid or heptadecafluorooctanesulfonic acid.

perfluorobenzene, hexafluorometaxylene and such polyfluoroaromatic compounds, perfluorotributylamine, perfluorotripropylamine and such polyfluorotrialkylamin compounds, perfluorohexane, perfluorooctane, (perfluoro-n-octyl) ethane, perfluoro-(2,3,5-trimethylhexane), and other such polyfluoroalkane compounds, (perfluoro-n-octyl) ethylene and such polyfluoroolefin compounds, perfluorocyclohexane, perfluorodecalin and such polyfluorocycloalkane compounds perfluoro-(2-butyltetrahydrofuran) and such polyfluorocyclic ether compounds; trichlorotrifluoroethane and such chlorofluorocarbons, 1,3-dichloro-1,1,2,2,3-pentafluoropropane, 1,1-dichloro-2,2,3,3,3-pentafluoropropane and such chlorofluorohydrocarbons, fluorine-containing low molecular weight polyethers, and the like.

1,1,2-trichloro-1,2,2-trifluoroethane, perfluoro (2-butyltetrahydrofuran) and perfluorohexane, perfluoro(2-butyl tetrahydrofuran) (Florinert FC-75, a product by Minnesota Mining and Manufacturing Co.), 1,1,2-trichloro-1,2,2-trifluoroethane (F-113), perfluoro(2-butyltetrahydrofuran), perfluorohexane, 1,1,2-trichloro-1,2,2-trifluoroethane, perfluoro (2-butyltetrahydrofuran) and perfluorohexane. 1,1,2-trichloro-1,2,2-trifluoroethane Florinert FC-40, FC-75, etc. (trade name; manufactured by 3M (K.K.)).

hexafluorobenzene, benzotrifluoride, bis(trifluoromethyl)benzene
pentafluorobenzene, 1,3-bis(trifluoromethyl)benzene or
1,4-bis(trifluoromethyl)benzene; a fluorine-containing alicyclic hydrocarbon
such as perfluorodecalin, perfluorocyclohexane or
perfluoro(1,3,5-trimethylcyclohexane); a fluorine-containing alkylamine such as
perfluorotributylamine or perfluorotripropylamine; a fluorine-containing cyclic
ether such as perfluoro(2-butyltetrahydrofuran), a fluorine-containing polyether
such as a fluorine-containing low molecular weight polyether; a
fluorine-containing ketone such as bis(heptafluoroisopropyl)ketone; as well as a
fluorine-containing aliphatic hydrocarbon such as perfluorohexane,

perfluoro carboxylic acid derivatives such as methyltrifluoro acetate,
ethyltrifluoro acetate and butylpentafluoro propionate;

hydrochlorofluorocarbons such as HCFC-123, HCFC-141b and HCFC-225.

"Aflood" (a fluorine-containing solvent by Asahi Glass Co., Ltd.).

fluorine-containing solvents such as
trichlorotrifluoroethane, monofluorotrichloromethane and the like.

other fluorine-substituted ketones, fluorine-substituted
esters, fluorine-substituted amides, fluorine-substituted ethers,
fluorine-substituted aromatic hydrocarbon and fluorine-substituted aliphatic
hydrocarbon.

1,1,2-trichloro-1,2,2-trifluoroethane,
1,1,2,2-tetrachloro-1,1-difluoroethane, (trifluoromethyl)benzene and
1,3-bis(trifluoromethyl)benzene

1,1,2-trifluorotrichloroethane, 1,2-difluorotetrachloroethane,
hexafluorometaxylene, 1,1,2,3,4-hexafluorotetrachlorobutane and the like.

a fluorine-containing solvent (Diflon Solvent S-3, produced by Daikin Kogyo Co., Ltd.)

octafluorodichlorobutane, 1,1,2-trifluoro-1,2,2-trichloroethane,
1,2-difluoro-1,1,2,2-tetrafluoroethane

fluorine-containing solvent is selected from the group consisting of fluorohalogenides; perfluoro alkanes; perfluoro alkenes; cyclic fluoride compounds; perfluorohydrides; perfluorocarboxylic acids; perfluoroketones; perfluoroaldehydes; perfluoroalcohols; perfluoroethers; amine fluorides; perfluorothiols; perfluorosulfonic acids; and organic-phosphorus compound-arsenic compound-fluorine derivatives.

vinyl fluoride; vinylidene fluoride; trifluoroethylene; chlorotrifluoroethylene (CTFE); 1,2-difluoroethylene; tetrafluoroethylene (TFE); hexafluoropropylene (HFP); perfluoro(alkyl vinyl) ethers such as perfluoro(methyl vinyl) ether (PMVE), perfluoro(ethyl vinyl) ether, and perfluoro(propyl vinyl) ether (PPVE); perfluoro (1,3-dioxole); perfluoro(2,2-dimethyl-1,3-dioxole) (PDD)

fluorinated solvent is selected from, the group consisting of perfluorotoluene, perfluorocyclohexane, perfluorodimethylcyclohexane, perfluoro-methylcyclohexane, perfluoroxylene, perfluorobenzene,

perfluorodecalin, perfluorodecane, perfluorohexane, perfluorooctane, perfluorodecane, trifluorotoluene, pentafluorotoluene and low molecular weight liquid polymers having the structure of fluorinated polyethers

dichlorodifluoromethane, 1,1-dichlorotetrafluoroethane, 1,2-dichlorotetrafluoroethane, 1-chloro-1,1-fluoroethane, 1-chloroheptafluoropropane, 1,1,1,2,2-pentafluoropropane, perfluorobutane, 2,3-di-chlorooctafluorobutane, and 2,2,3,3-tetrafluorobutane. Preferred solvents include butane, pentane, 1,1-dichloro-1-fluoroethane, and

1,2-dichlorotetrafluoroethane; perfluoroisooctane, perfluorotributylamine,

perfluoroheptane,

perfluorinated 2-butyltetrahydrofuran

perfluorohexane, perfluorotributylamine, perfluorotriethylamine,

fluorinated alkenes such as pentafluorostyrene, octafluorostyrene,

perfluoro-1,4-pentadiene, perfluoro-1,6-heptadiene, 3,5-bis(trifluoromethyl)

styrenes, etc.; fluorinated acrylates and methacrylates such as

2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl acrylate,

2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl methacrylate,

2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-nonadecafluorodecyl methacrylate,

1,2,2,3,3,4,4,5,5,6,6-undecafluorocyclohexylmethyl acrylate,

1,2,2,3,3,4,4,5,5,6,6-undecafluorocyclohexylmethyl acrylate,

1,2,2,3,3,4,4,5,5,6,6-decafluoro-4-trifluoromethylcyclohexylmethyl acrylate,

perfluorohexyl acrylate, perfluorobutyl acrylate, perfluorodecyl acrylate,

2,2,2-trifluoroethyl acrylate, 2,2,2-trifluoroethyl methacrylate,

1,1,1,3,3,3,-hexafluoro-2-propyl acrylate, $\text{C}_8\text{F}_{17}\text{SO}_2\text{N}(\text{n-C}_4\text{H}_9)\text{CH}_2\text{CH}_2\text{O}_2\text{CCH}=\text{CH}_2$,
etc; trifluorinated alkyl acrylonitriles, e.g., trifluoromethyl acrylonitrile;
perfluoroalkyl vinyl ethers such as perfluorobutyl vinyl ether, pentafluoroethyl
vinyl ether, ...

Any combination of the above solvents. It is found as is shown in the experimental section that when polyaniline is processed in certain combination of the above solvents that higher conductivity is attained than that from the corresponding individual solvents.

The above fluorinated solvents can be used with mixtures with non fluorinated solvents including nonfluorinated alcohols, phenols, esters, ethers, ketones, amides, amines, alkanes, cyclic alkanes, alkenes, aromatics, and so on such as anisole, benzyl alcohol, cyclohexanone, ethyl lactate, ethyl acetate, diethyl ketone, diethyl malonate, m-cresol, phenol, N-methylpyrrolidinone, N-dimethylformamide, propylene glycol dimethyl ether acetate, isopropanol, ethanol, water, dimethylpropylene urea, gamma butyrolactone, diethylether, benzene, toluene, chloroform, tetrahydrofuran, heptanone, pentanones, and so on.

EXAMPLES:

The unsubstituted polyaniline in the emeraldine form is synthesized by the chemical oxidative polymerization of aniline in 1N HCl using ammonium peroxydisulfate as an oxidizer. Polyaniline can also be oxidatively polymerized electrochemically as taught by W. Huang, B. Humphrey, and A.G. MacDiarmid, J. Chem. Soc. Faraday Trans. 1, 82, 2385, 1986. In the chemical synthesis, the conducting polyaniline hydrochloride (hydrochloride) salt precipitates from solution. The

polymerization is allowed to proceed for several hours after which the powder is filtered, washed with excess 1N hydrochloric acid. The emeraldine hydrochloride is then converted to non-conducting or non-doped emeraldine base by reaction with 0. ammonium hydroxide. The emeraldine base is then filtered, washed with ammonium hydroxide, then washed with methanol and dried. The polymer at this stage is in the undoped emeraldine base form as a powder

Substituted (either on the aromatic ring or on the nitrogen) polyanilines in the emeraldine form are synthesized in the fashion as above but using the appropriate substituted aniline monomer in the polymerization reaction. Copolymers are made by the oxidative polymerization of one or more monomers. acids can also be used in the polymerization reaction other hydrochloric acid. Aqueous acetic acid, sulfuric acid, organic sulfonic acids, such as aqueous toluenesulfonic acid, dodecylbenzenesulfonic acid, camphorsulfonic acid, and so on The o-ethoxy substituted polyaniline was prepared by polymerization of o-ethoxy aniline in 1N hydrochloric acid described above. Copolymers having various amounts of o-ethoxy content were synthesized by polymerizing o-ethoxyaniline and aniline in aqueous 1N hydrochloric acid. The amount of o-ethoxy content in the final polymer was controlled by varying the feed ratio of this monomer in the initial polymerization reaction Other substituted derivatives such as the substituted polyaniline as described in US application number 08/595,853 filed on 2/2/96 entitled "Cross-Linked Electrically Conductive Polymers and Precursors Thereof" and US application serial number 08/594,680 filed on 2/2/96 entitled "Methods of Fabricating Cross-Linked Electrically Conductive Polymers and Precursors Thereof" the teachings of which are incorporated herein by reference.

The substituted and unsubstituted emeraldine base powder is generally processed by dissolving the powder in an organic solvent and mechanically stirring the admixture to form a solution. The solution can be used to spin-coat films of the emeraldine base polymer on silicon wafers, quartz wafers, salt plates, and so on. These films were on the order of 500 Å to 1.0 μm. Thicker films (on the order of 50 to 200 μm) were made by solution casting techniques in the

869000" 0915000

solution was poured into an aluminum pan or glass dish and placed in a vacuum oven at 60 C for 24 hours. The solution can also be used to process the material into a structural part or into a fiber. The substituted emeraldine base such as the o-ethoxy substituted emeraldine base was more soluble than the unsubstituted emeraldine base. This polymer can be dissolved in cyclohexanone, tetrahydrofuran, ethyl lactate and so on. A solution was made in cyclohexanone (5% solids) and this solution was used to process films (thin and thick).

The base form of the material is made conducting by adding a dopant to the base solution and allowing the reaction to stir over night. The dopant can be added to the solvent in conjunction with the base polymer and allowed to react overnight. In addition, the dopant can be added to the solvent first, dissolved, then adding the base form of the polymer and allowing the reaction to proceed overnight. In addition, structural parts, films, or fibers can also be processed from these conducting polymer solutions.

Specific Examples:

Emeraldine base was added to a 50/50 mixture of hexafluoroisopropanol/hexafluorophenylpropanol and allowed to stir for 1 hour at which time the dopant was added. The reaction was allowed to react overnight. Upon addition of the dopant, a green solution was attained. After the reaction was completed, the reaction solution was filtered through 0.2um filters. The solutions were used to spin coat excellent films having conductivity ranging from 100 to 200 S/cm. It was noticed that the conductivity dependent on the concentration of the polymer in solution. From a .5 to 2% solution, a conductivity of 100 S/cm was attained and above 3% a conductivity of 200 S/cm was attained. At the low % concentrations, the polymer is highly solvated and the solution basically consists of highly solvated chains with minimal interactions between chains. At the higher concentration, the chains are well solvated but there is still some interchain interactions which facilitate the interchain mobility. The UV of the above material in this 50/50 mixture is shown in Figure 3. As can be seen, a highly delocalized polaron absorption is attained indicating highly delocalized carriers.

The dopant was camphorsulfonic acid and acrylamidopropane sulfonic acid. Other dopants include other suitable acids such as sulfonic acids, carboxylic acids, phosphonic acids and so on.

The same reaction was carried out in NMP with the same dopants. The conductivity for these films was on the order of 10^{-2} S/cm (4 orders of magnitude less than that observed with the fluorinated solvent mixtures). The UV of this material is shown in Figure 4. In contrast to the same material processed in the fluorinated solvent mixtures, this exhibits a localized polaron absorption peak indicating less delocalized carriers.

The above reaction was carried out in a number of solvents in a similar way. Table I shows the conductivities that result in the various solvents. This table is only exemplary and not limiting.

The polyanilines processed with these new solvents that give conductivities between 100 and 200 S/cm was tested in the form of coatings on various plastic sheets such as polycarbonate, petg, nylon, and PVC for EMI shielding in a TEM cell. Shielding was studied between 50 and 1000 MHz. Table 2 gives the results for these coatings. As can be seen, high conductivity polyaniline gives attenuation levels in the 30 to 40 db level.

These films are also applicable for electrodes for displays (light emitting diodes, liquid crystal displays) contacts for devices such as transistors. They can be used for resists, ESD protection, corrosion protection, and EMI shielding. The solutions are stable and give rise to excellent quality films with high clarity and transparency.

The ethoxysubstituted polyaniline as well as copolymers with aniline was also doped in these solvents as was the hydroxyethyl substituted polyanilines and copolymers with aniline.

Some of these materials together with the corresponding conductivity is given in Table 1.

These solvents interact with the polyaniline, solvating and deaggregating the chains. This allows the chains to expand. A true solution is approached. This accounts for the high quality films and high transparency. A concentration effect on the conductivity is observed. As the concentration of the polymer decreases, a solution is approached consisting of highly solvated chains with very little interactions between chains. As the concentration increases, some interchain interactions are present which help interchain carrier mobility. Fig. 5 shows this effect as it depicts the ultraviolet/visible/near IR spectra for a doped polyaniline material processed in hexafluoroisopropanol at 1 and 2%. At 2%, the localized polaron absorption is stronger than it is at 1% indicating that at 1%, most of the chains are effectively solvated minimizing interchain interactions.

These highly conducting polymers can be blended with other conductors or other thermoplastic or thermoset resins.

The teachings of all references cited herein are incorporated by reference herein.

While the present invention has been described with respect to preferred embodiments, numerous modifications, changes, and improvements will occur to those skilled in the art without departing from the spirit and scope of the invention.

CLAIMS

What is claimed is:

1. A method comprising:

processing a polymer selected from the group consisting of a precursor to an electrically conductive polymer and an electrically conductive polymer in a solvent comprising a fluorinated solvent.

2. A method according to claim 1 wherein said polymer is in a solution of said fluorinated solvent and less than about 20 weight % of said solution.

3. A method according to claim 1 wherein said precursor polymers to said electrically conductive polymers are selected from the group consisting of substituted and unsubstituted polyparaphenylenes, polyparaphenylenevinyls, polyanilines, polyazines, polythiophenes, polythianaphthenes, polyphenylenesulfides, polyfurans, polypyrroles, polyselenophenes, polyacetylenes and combinations thereof and copolymers of monomers thereof.

4. A method according to claim 1 wherein said processing is selected from the group consisting of synthesizing said polymer in said solvent and solvating said polymer in said solvent.

5. A method according to claim 1 wherein said polymer is a precursor to an electrically conductive polymer and exposed to said solvent while said precursor is exposed to a dopant.

6. A method of forming a polymer selected from group consisting of a precursor to an electrically conductive polymer and an electrically conductive polymer comprising: exposing a solution of polymerizable units to a solvent comprising a fluorinated solvent during polymerization to form said polymer.

7. A method comprising:

polymerizing monomers in the presence of a solvent comprising a fluorinated solvent to form an electrically conductive polymer; during neutralization of said electrically conductive polymer to an undoped form to form a deaggregated nondoped form of said electrically conductive polymer.

8. A method according to claim 1 wherein said solvent comprises a combination of said fluorinated solvent and a nonfluorinated solvent.

9. A method according to claim 1 wherein said polymer is in a solution and is less than about 5 weight percent of said solution.

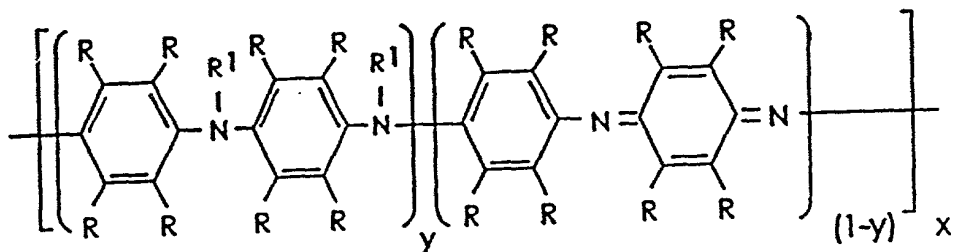
10. A method according to claim 6 wherein said polymerizable units are selected from the group consisting of one or more of monomers and oligomers.

11. A method according to claim 1 wherein said polymer is in a form selected from the group consisting of a solution and a solid state.

12. A method according to claim 1 wherein

13. A method according to claim 1 wherein said polymer is a polyaniline.

21. A method according to claim 1 wherein said polymer is polyaniline having structural formula:



wherein each R can be H or any organic or inorganic radical; each

R can be the same or different; wherein each R

sup 1

can be H or any organic or inorganic radical, each R

sup 1

can be the same or different;

$x \geq 1$

; preferably

$x \geq 2$

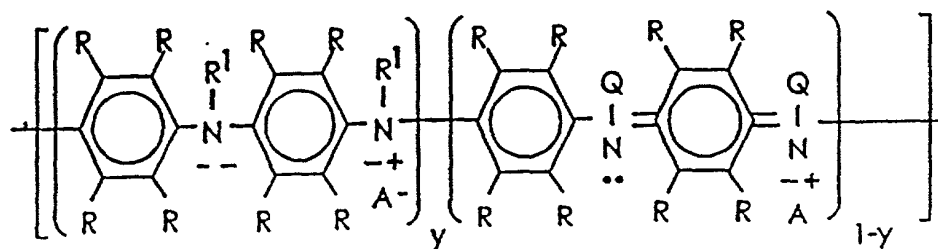
;y has a value of 0.5 or said nonreduced or nonoxidized form; y

has a value from greater than 0.5 to 1 for said reduced form and

y has a value from less than 0.5 to 0 said oxidized form.

22. A method according to claim 1 wherein said polymer is a

polyaniline having structural formula:



wherein each R can be H or any organic or inorganic radical; each

R can be the same or different; wherein each R

sup 1

can be H or any organic or inorganic radical, each R

sup 1

can be the same or different;

$x \geq 1$

; preferably

$x \geq 2$

y has a value of 0.5 or said nonreduced or nonoxidized form; y

has a value from greater than 0.5 to 1 for said reduced form and

y has a value from less than 0.5 to 0 said oxidized form.

23. A method according to claim 1 wherein said solvent comprises more than one fluorinated solvent.

24. A method according to claim 1 further including forming from said polymer an object selected from the group consisting of a film, a fiber, or a structural part.

25. A method according to claim 1 wherein an electrically conducting polymer is formed having a level of electrical conductivity thereof which is varied by varying the concentration of said polymer in said solution.

25. A method according to claim 1 wherein an electrically conducting polymer or precursor is blended with a thermoset or thermoplastic polymer.

**METHODS OF PROCESSING AND SYNTHESIZING ELECTRICALLY
CONDUCTIVE POLYMERS AND PRECURSORS THEREOF TO FORM ELECTRI-
CALLY CONDUCTIVE POLYMERS HAVING HIGH ELECTRICAL CONDUCTIVITY**

ABSTRACT OF THE DISCLOSURE

The present invention is directed to methods of solvating electrically conducting polymers and electrically conducting polymers by processing these materials in selected solvents comprising at least one of the solvents being a fluorinated solvent. High solubility and conductivity in the hundreds of S/cm are achieved by these methods. Excellent coatings are attained. These materials have application in EMI shielding, electrodes for displays, contacts for devices, ESD protection, corrosion protection and resists.

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Table 1

Emeraldine Base Doped with
Camphorsulfonic Acid or Acetamidopropene sulfonic
acid

<u>Solvent</u>	<u>Concentration</u>	<u>Conductivity</u>
Trifluoroacetic acid	1%	75 S/cm
	2%	7100 S/cm
Hexafluoroisopropanol	1%	75 S/cm
	2%	100 S/cm
	3%	7100 S/cm
Hexafluoroisopropanol / 50	1%	100 ⁰ S/cm
Hexafluorophenylpropanol 50	2%	200 S/cm
Hexafluoroisopropanol (HFIP) / Tetrafluoropropanol (TFP) 25/75	3%	100 S/cm
HFIP/TFP 50/50	3%	200 S/cm
HFIP/TFP 75/25	3%	170 S/cm
HFIP/TFP 63/37	3%	130 S/cm

perfluoro butyl alcohol	390	120 $\frac{1}{\text{cm}}$
2,3,5,6, tetrafluorophenol	390	200 $\frac{1}{\text{cm}}$
Tetra fluoro propenol	390	40 $\frac{1}{\text{cm}}$
Hexafluorophenyl propenol / cyclohexanone	390	75 $\frac{1}{\text{cm}}$
Hexafluorophenyl propenol / anisole	390	75 $\frac{1}{\text{cm}}$
4- (trifluoromethyl) benzyl alcohol	"	50 $\frac{1}{\text{cm}}$
2,4 difluorobenzyl alcohol	"	75 $\frac{1}{\text{cm}}$
4- fluorobenzyl alcohol	"	75 $\frac{1}{\text{cm}}$
Hexa fluoro propenol / benzyl alcohol	"	75 $\frac{1}{\text{cm}}$
Hexafluorophenyl propenol / benzyl alcohol	"	140 $\frac{1}{\text{cm}}$
HFIP / pentafluoro propenol	50/50	"

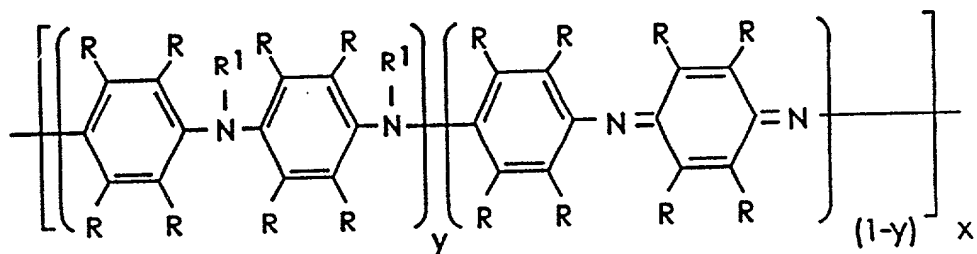
Table 2

Mater.	Frequency (MHz)										
	50	100	200	300	400	500	600	700	800	900	1000
S.C. 2um	30	26	24	20	20	10	20	15	18	15	18
S.C. 3um	30	28	24	20	22	12	20	18	17	16	19
R.C. 1x 1-2	30	27	23	19	18	8	14	12	14	14	17
R.C. 1x 4um	36	36	40	36	22	25	30	26	30	37	30
R.C. 2x 3um	33	33	35	30	25	27	32	25	31	30	30
R.C. 1x 4um	35	34	36	38	32	30	32	26	32	30	31

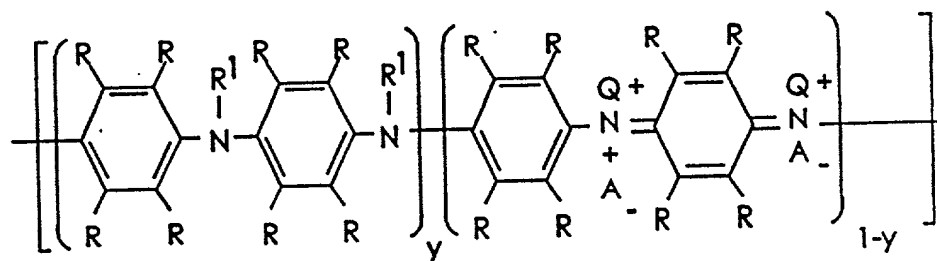
All values are in dB

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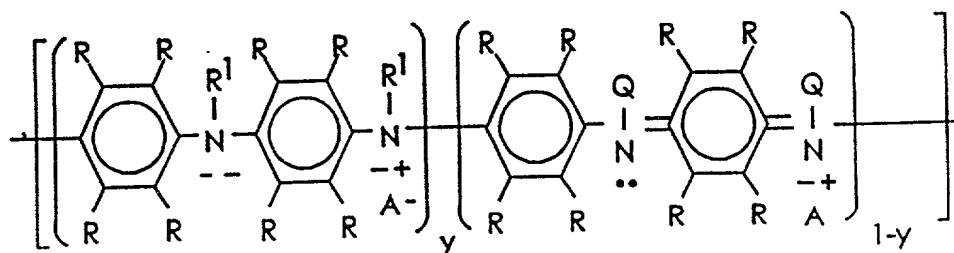
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FIG. 2

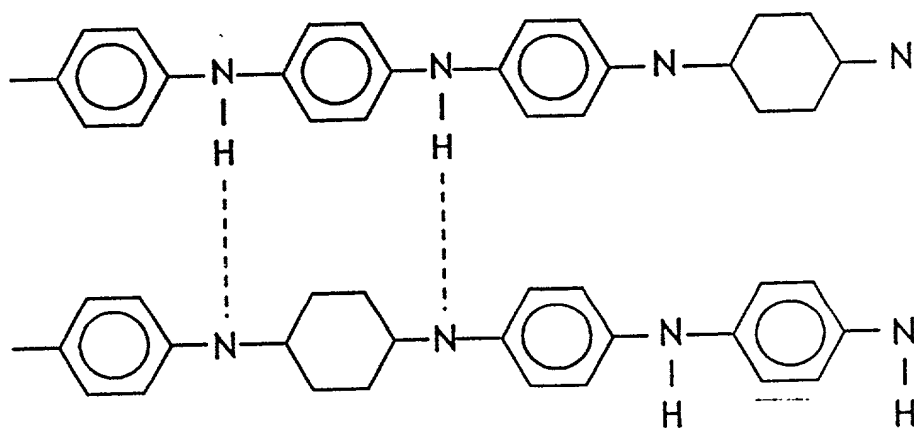
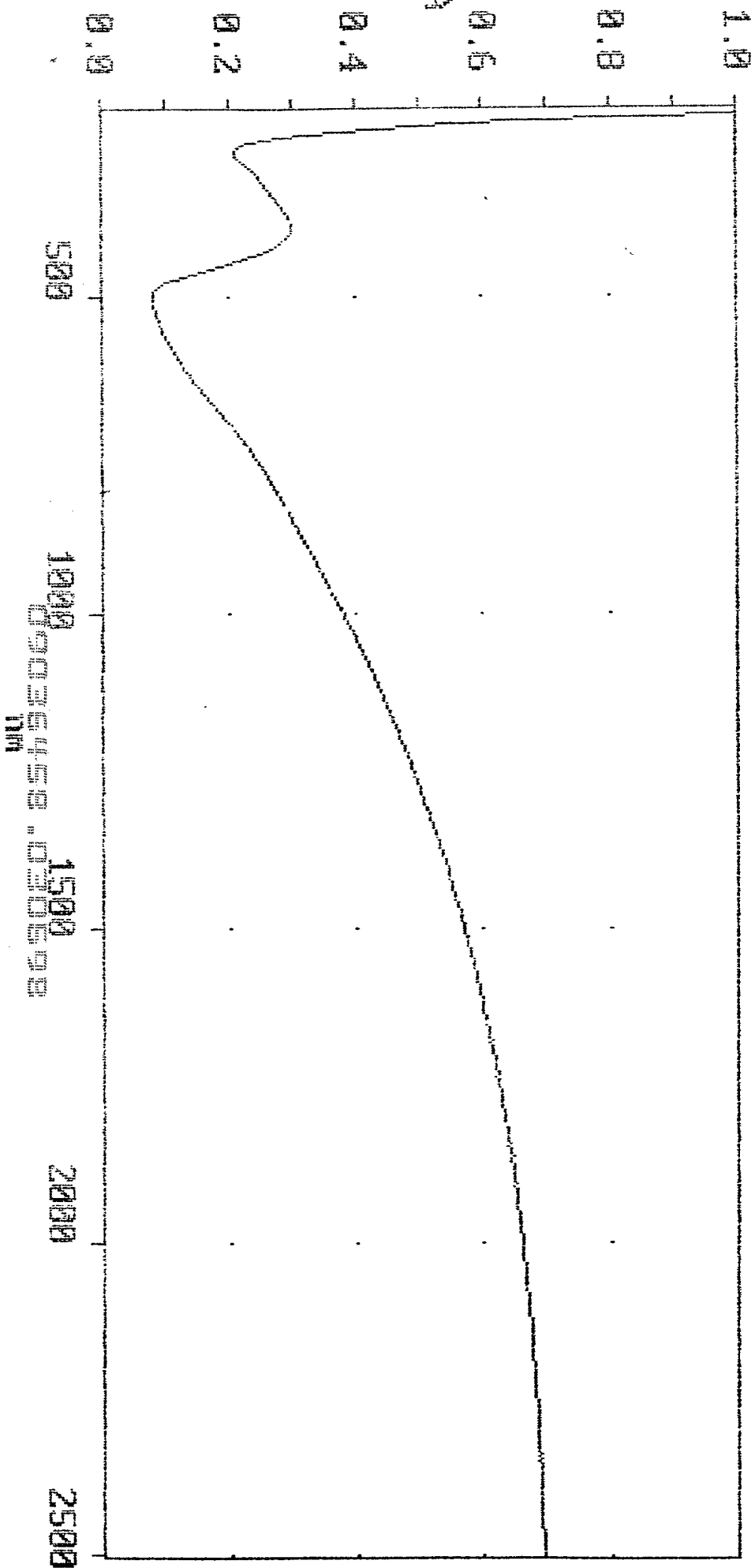


Figure 3

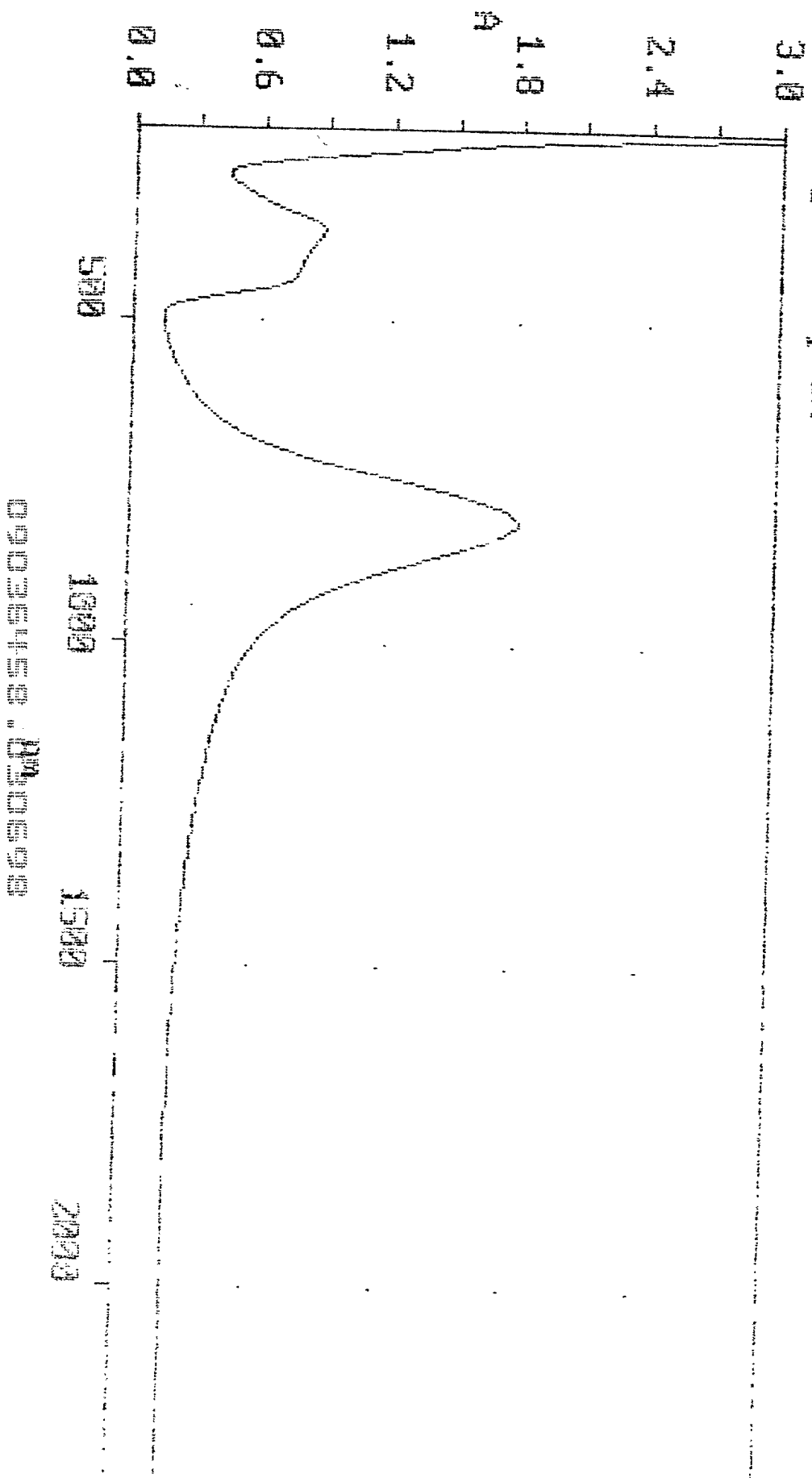
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: mastm2: 2500.0 - 200.0 nm; pts 2301; int 1.00; ord 0.0042 - 1.4959 A
n1: eb in h1p/hexa .5% acry



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Figure 4

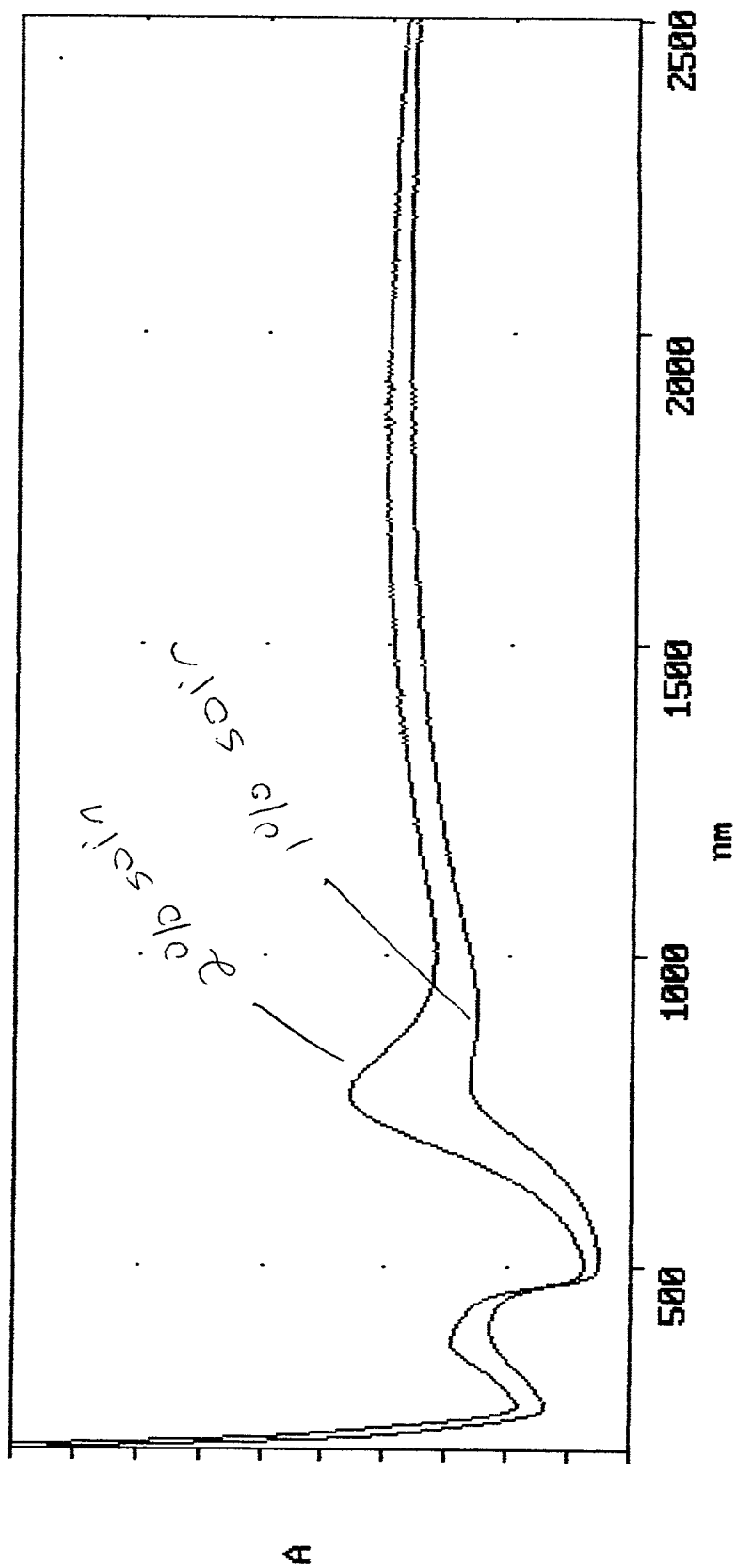
X: mastm; 2500.0 - 200.0 nm; pts 2301; int 1.00; ord 0.1479 - 3.5150 A
Inf: eb acry in mp 5%

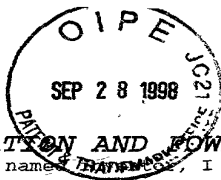


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Fig 5

X: mahfapro; 2500.0 - 200.0 nm; pts 2301; int 1.00; ord 0.1636 - 2.8317 A
Inf: pani acryl in hfip 1 $\frac{1}{2}$ (1:2.0)



**DECLARATION AND POWER OF ATTORNEY FOR PATENT APPLICATION**As a below named Manny W. Schechter, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name;

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

METHODS OF PROCESSING AND SYNTHESIZING ELECTRICALLY CONDUCTIVE POLYMERS AND PRECURSORS THEREOF TO FORM ELECTRICALLY CONDUCTIVE POLYMERS HAVING HIGH ELECTRICAL CONDUCTIVITY

the specification of which (check one)

☐ is attached hereto.☒ was filed on March 6, 1998 asApplication Serial No. 09/036,458and was amended on _____
(if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, Section 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)	Priority Claimed
(Number) _____ (Country) _____ (Day/Month/Year Filed) _____	<input type="checkbox"/> Yes <input type="checkbox"/> No
(Number) _____ (Country) _____ (Day/Month/Year Filed) _____	<input type="checkbox"/> Yes <input type="checkbox"/> No
(Number) _____ (Country) _____ (Day/Month/Year Filed) _____	<input type="checkbox"/> Yes <input type="checkbox"/> No

I hereby claim the benefit under 35 U.S.C. §119(e) of any United States provisional application(s) listed below.

(Application Number) _____	(Filing Date) _____
(Application Number) _____	(Filing Date) _____

I hereby claim the benefit under Title 35, United States Code, Section 120 of any United States Application(s) listed below and, insofar as the subject matter of each of the claims of the application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, Section 112, I acknowledge the duty to disclose information material to the patentability of this application as defined in Title 37, Code of Federal Regulations, Section 1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application;

(Application Serial No.) _____	(Filing Date) _____	(Status) (patented, pending, abandoned) _____
(Application Serial No.) _____	(Filing Date) _____	(Status) (patented, pending, abandoned) _____

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY: As a named inventor I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith (list name and registration number).

Manny W. Schechter (Reg. No. 31,722), Terry J. Ilardi (Reg. 29,936), Christopher A. Hughes (Reg. 26,914), Edward A. Pennington (Reg. 32,588), John E. Hoel (Reg. 26,279), Joseph C. Redmond, Jr. (Reg. 18,753), and Daniel P. Morris (Reg. 32,053).

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Inventor's signature

Date

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Post Office Address

Full name of fifth joint inventor, if any

Inventor's Signature

Date

Residence

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Full name of sixth joint-inventor, if any

Inventor's signature

Date

Residence

Citizenship

Post Office Address

Full name of seventh joint-inventor, if any

Inventor's signature

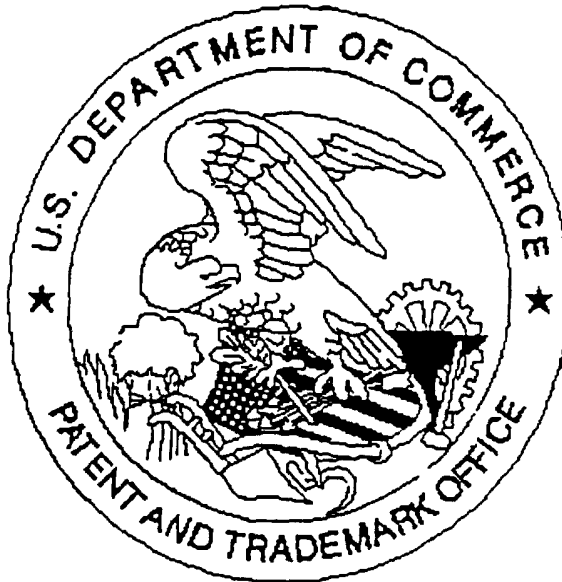
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